

• Volume 10A, Number 2, June 1961

BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL

Section A CHEMISTRY

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THE INFLUENCE OF POTASSIUM ON THE UPTAKE OF SODIUM BY PLANTS UNDER SALINE CONDITIONS

H. HEIMANN AND R. RATNER

Department of Chemistry, Technion-Israel Institute of Technology

Salinity is a wide-spread condition in the arid and semi-arid zones of the world. It is mostly caused by the rise of a saline ground water table, or by the application of saline irrigation water. Generally sodium is the main cation involved in salinity. Whereas the damage caused to crops by sodium was formerly attributed only to its deflocculating influence on soil structure, today the view that sodium taken up in excessive amounts may also directly disturb plant life is becoming more widely accepted. In animal physiology sodium always occurs together with potassium. The antagonistic relationships between these two ions come into play in the action of nerves and muscles. In the behaviour of organized cell systems belonging to plants one may analogously expect an antagonism between sodium and potassium. Surprisingly the accepted textbooks of plant physiology and agronomy do not mention the existence of such an antagonism and limit themselves to discussion of other antagonistic pairs of cations, such as potassium versus calcium or magnesium. With regard to sodium and its role in plant production the discussion centres around two points, namely: whether sodium is an essential plant nutrient for commercial crops, and secondly, to what extent the expensive potassium fertilizers might be replaced by much cheaper sodium compounds.

Heimann⁶ stressed the fallacy of this approach. Discarding the notion of plant nutrition, he re-evaluated the relationships between sodium and potassium on the basis of the environment concept. These relationships have an ambivalent character, synergistic as well as antagonistic, depending on the circumstances. In a saline environment where high concentrations of sodium are encountered, antagonism is predominant. Field observations of successful farming with highly saline water containing some potassium, indicated a protective influence of this element on plants exposed to saline conditions. It accordingly appeared desirable to study how far the uptake of sodium might be prevented by the presence of potassium as its antagonist.

The literature contains many figures lending themselves to an interpretation in this sense, for example:

Bower and Pierre³ reported pot experiments with flax and oats on a slightly saline high-lime soil. Increasing dressings with KCl depressed the uptake of sodium proportionally and raised the yield. They contrasted this green-house result with the lack of response to potassium by the same crop grown in fields on a normal soil of the same type. The soil analyses show a much higher percentage of

exchangeable potassium in the latter case, i.e. 0.54 m.e. per 100g against 0.17 m.e. per 100g in the pot experiments. This difference explains the observed facts.

*Reisenberg and Rosovsky*¹³ who grew barley seedlings by the Neubauer method in solutions of up to 72 m.e. per litre of sodium chloride, found the absorption of sodium distinctly reduced by the presence of potassium added at different levels. They related this result to the problem of salinity and stated: "If this result is corroborated in further experiments, it may prove to be of practical significance and application wherever salty irrigation water is used".

*Van Itallie*⁹ described pot experiments with oats in a soil artificially saturated by exchangeable bases in different ratios. His conclusion was that the potassium percentage is the main factor determining the uptake of sodium by the growing plant, whereas the uptake of potassium depends only on the potassium concentration in the soil.

*Lunt and Nelson*¹², who tried to evaluate sodium as a potassium substitute in growing cotton, found that sodium had little effect on the absorption of potassium except when the plant became mature. On the other hand, the absorption of sodium was reduced by increasing the level of potassium.

*Barbier and Chabannes*² dealt with the special problem of sodium accumulation in roots, using peas and white mustard as test plants. Their nutrient solution contained 0.6 m.e. per litre of sodium, a rather low salinity. On increasing the potassium concentration from 0.1 m.e. per litre to 5.0 m.e. per litre the sodium content of the peas dropped from 155 to 7.6 m.e. per 100g in the roots, and from 16.0 to 2.1 m.e. per 100g in the stems and leaves. Calcium on the other hand had only a minor influence on the uptake of sodium. They concluded that the antagonism of calcium was less marked than that of potassium against the absorption of sodium.

*Larson and Pierre*¹¹ reported figures for the sodium uptake by oats on two different kinds of soils which clearly indicate a reduction produced by moderate additions of potassium.

*Kohl, Kofranek, and Lunt*¹⁰ grew african violets (*Saintpaulia*) in solutions with up to 23.6 m.e. per litre of sodium and found lowest values for sodium in the leaves at the highest concentration of potassium (3 m.e. per litre).

*Sankaranarayanan and Verghese*¹⁵ experimented with sunnhemp in sand culture. They observed a decrease of sodium in the tissue with increase of potassium in the medium, but sodium did not influence the potassium content.

*Huffaker and Wallace*⁷ used radioactive Na²² "to learn if potassium would effectively exclude sodium from plants, since a degree of sodium exclusion is sometimes of importance in agricultural practice". In their experiments very high concentrations of potassium, in the magnitude of 40 m.e. per litre, were needed to exclude sodium in corn and soybean grown in a solution containing 10 m.e. per litre of sodium. They claimed that differences in plant species are more important than the potassium level in determining the amount of sodium in the aerial parts of the plant, whereas with respect to the roots the potassium level controls the uptake of sodium.

Their conclusion is that "potassium and sodium absorption are competitive. Both appear to be bound at the same site in the root. A natural mathematical consequence is that the higher the Na-level the more difficult it is to effectively exclude it from plants by the use of K". As this result is contradictory to the other findings in the present review, it may be remarked that the experiments were carried out at most unnatural conditions of growth. In the first three weeks no sodium was present in the growth medium; then the plants were transferred to the experimental solutions containing sodium and left there for 48 hours only. Normal behaviour of living structures cannot be expected under those conditions. The results appear to be of limited validity.

*Huffaker and Wallace*⁸ continued their studies with other plant species. The figures reported for the absorption of sodium by citrus jambhiri indicate a definite decrease in leaves and roots produced by relatively small additions of potassium. But this result too appears to be of limited scope, for the reason given above.

*Bange*¹ studied the interactions in potassium and sodium absorption with maize seedlings in nutrient solutions, applying the continuous flow technique. He found that sodium absorption was strongly inhibited by excess potassium but only part of the potassium absorption was inhibited by excess sodium. These findings are interpreted in terms of the carrier hypothesis without relating them to agricultural practice.

*Scharrer and Mengel*¹⁶ worked with six different species of dicotyledons in studying the influence of radical and extraradical application of potassium on the cation distribution in the plant. They found a decrease of sodium in the leaves as well as in stems and roots on increasing the potassium level in the nutrient solution. On foliar application of potassium a reduced content of sodium in the leaves was observed, without a change in stems and roots. This observation appears to show a way of avoiding foliar salinization, while using sprinkler irrigation.

*Effmert*⁵ investigated the role of sodium as plant nutrient with carrots, wheat and beans. Whereas the addition of sodium caused an increase in the uptake of potassium, in accordance with the views expressed by Heimann⁶, a dressing with potassium decreased the absorption of sodium in all cases.

Although this literature survey is not exhaustive, enough evidence is given to strengthen the opinion that the absorption of sodium by plants can be kept in check by proper application of potassium.

The following experiments, were carried out to test the assumption on a more quantitative basis.

METHODS

The growth experiments were performed in pure quartz-sand, irrigated with solutions of varying composition as detailed in Table I. The concentration of sodium was from 10 to 60 m.e. per litre and that of potassium from 2.5 to 10 m.e. per litre. In all cases, the concentration of sodium was far above that of potassium as is usually the case in farming under saline conditions. Maize, tomato, and sunflower served as

TABLE I
Composition of solutions used for irrigation in milliequivalents per litre

No.	Na ⁺	K ⁺	Ca ⁺⁺	Cl ⁻
1	6	2.5	2	—
2	10	2.5	2	4
3	10	5	2	6.5
4	20	2.5	4	16
5	20	5	4	18.5
6	20	10	4	23.5
7	40	2.5	8	40
8	40	5	8	42.5
9	40	10	8	47.5
10	40	20	8	57.5
11	60	2.5	12	64
12	60	5	12	66.5
13	60	10	12	71.5
14	60	20	12	81.5
15	60	30	12	91.5

In addition all the solutions contained 2.0 m.e. Mg⁺⁺, 8.0 m.e. NO₃⁻, 2.5 m.e. H₂PO₄⁻, 2.0 m.e. SO₄⁼ per litre, and 1 c.c. of Hoagland's A-Z solution.

test plants. All the seeds were germinated under identical conditions in quartz-sand impregnated with solution No. 1. The tomato seedlings were transferred to pots after 12 days, and those of maize and sunflower after 6 days of germination. Each pot contained 3.5kg of sand and received one plant only. There were five replicas of each formula. The pots, altogether 225, were distributed at random and inserted into the soil. The experiments were carried out in the rainless season. 1.5 litres of the appropriate solution was allowed to percolate through each of the pots once every three days. Loss of water by evaporation was compensated for by adding tap water three times daily. This water contained 6 m.e. per litre of calcium, 1.8 m.e. per litre of sodium and only minute amounts of potassium. The plants were cropped 35 days after their transfer to the pots.

The whole plants were dried at 105°C, and organic matter was then destroyed by the wet combustion method. Sodium, potassium, and calcium were determined with the flame photometer.

RESULTS AND DISCUSSION

The results are summarised in graphs nos. 1-6. Graphs nos. 1-3 deal with the influence of potassium on the uptake of sodium at four different levels of salinity, and graphs nos. 4-6 vice versa with the influence of sodium on the uptake of potassium present at three different levels. Sodium was taken up by the three tested plants in

extremely different degrees. The tomato plants at the highest level of salinity in the growth medium absorbed sodium up to 380 m.e. per 100g dry weight, whereas under the same conditions the sunflower plants absorbed only 21 m.e. per 100 g dry weight. The absorption of sodium by maize reached an intermediate level of 125 m.e. per 100 g dry weight. With respect to the absorption of potassium the differences between

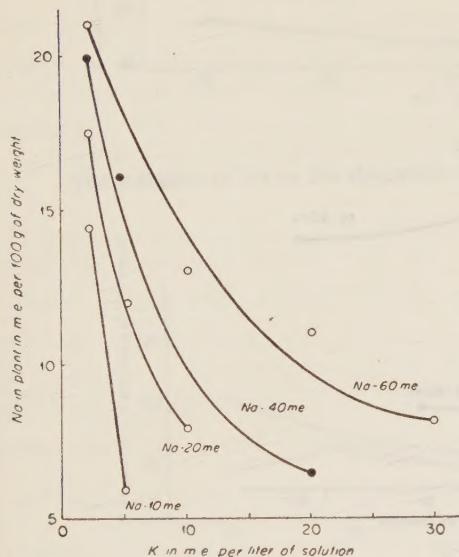


Figure 1
The influence of K on the absorption of Na by sunflower plants at different levels of Na

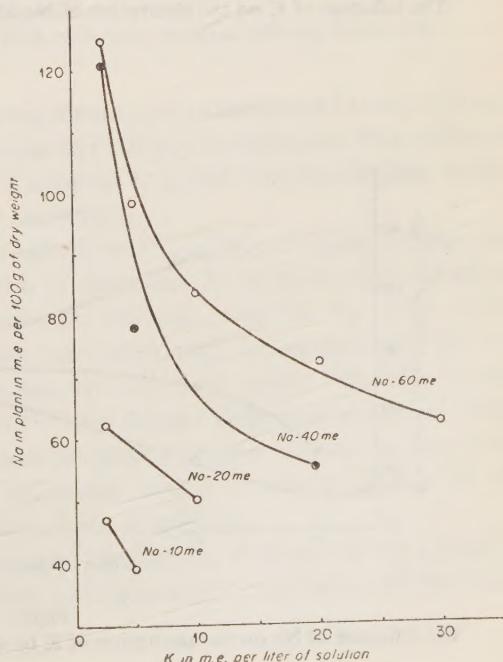


Figure 2
The influence of K on the absorption of Na by maize plants at different levels of Na

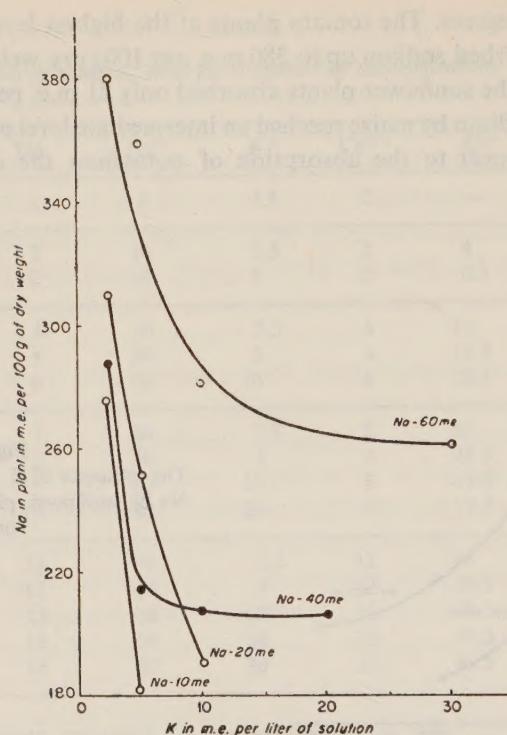


Figure 3

The influence of K on the absorption of Na by tomato plants at different levels of Na.

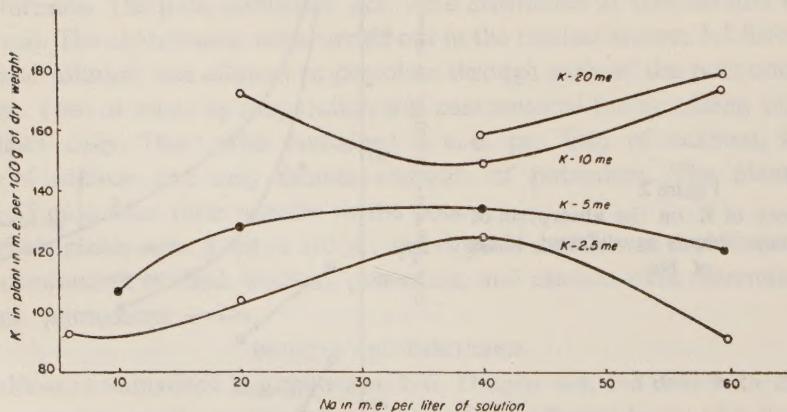


Figure 4

The influence of Na on the absorption of K by sun-flower plants at different levels of K.

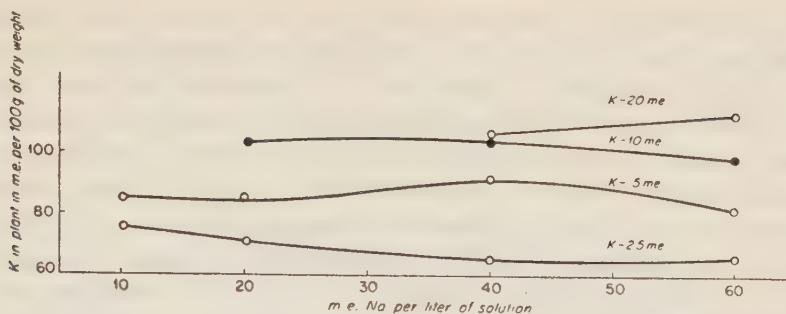


Figure 5

The influence of Na on the absorption of K by maize plants at different levels of K.

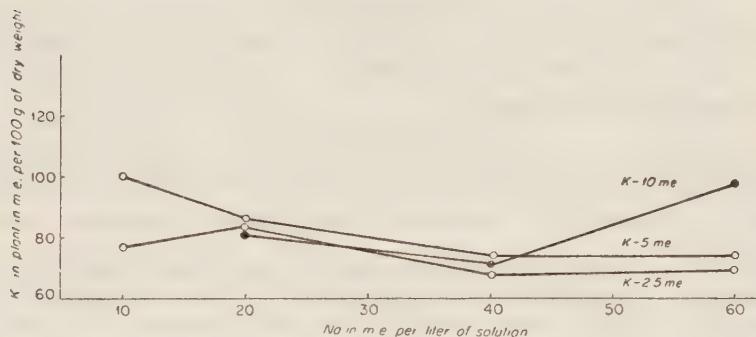


Figure 6

The influence of Na on the absorption of K by tomato plants at different levels of K.

the three kinds were rather small. The maximum uptake fluctuated between 100 m.e. per 100g dry weight by tomatoes and maize and 165 m.e. by sunflower. This differential behaviour of plants in the uptake of minerals is in line with the findings published by Collander and by many other investigators.

The uptake of sodium at all levels of salinity and by all plants tested (graphs nos. 1-3) was strongly influenced by addition of potassium to the percolating solutions. These results are in accordance with the findings reported by Van Itallie, although in his experiments the cations were introduced beforehand with the base exchange complex of the soil and oats was the only plant tested. They also confirm the claims by Reifenberg and Rosovsky¹³ who limited their experiments to barley seedlings and to rather narrow ratios between potassium and sodium. In our experiments relatively small increments of potassium caused a strong decline in the absorption of sodium, especially at high levels of salinity.

The uptake of potassium on the other hand (graphs nos. 4-6) was mainly a function of the level of potassium in the medium and apparently independent of the simultaneous presence of sodium.

These results strongly support the assumption that plants grown under saline conditions can be protected effectively against the detrimental intrusion of sodium into their tissues by ensuring a proper level of potassium in the growth medium. Figures for a balanced sodium-potassium ratio may be derived from our results for the growth of plants in nutrient solutions only, as in solutions a homogeneous array of ions is maintained. For growth in soils, however, the balanced ratio between the two cations cannot be defined by figures, as the potassium in soils appears in different and steadily changing states of availability. Nevertheless the general statement seems to be justified that under saline conditions the "nutritional" needs for potassium should be complemented by those required for its protective effect. The quantities concerned and the mode of application should be determined in every case by experiments in the field.

ACKNOWLEDGEMENT

Special thanks are due to Miss M. Shaltiel for her skillful assistance in these experiments and to Mr. Avram Even-Chaim of the Ruppin Agricultural School for his hospitality and good counsel.

REFERENCES

1. BANGE, G.G.J., 1959, Interactions in the potassium and sodium absorption by intact maize seedlings, *Plant and Soil*, **11**, 17-29.
2. BARBIER, G. AND CHABANNES, J., 1951, Accumulation of sodium in the roots of plants, *C.R.*, **232**, 1372-1374.
3. BOWER, C.A. AND PIERRE, W.H., 1944, Potassium response of various crops in a high lime soil in relation to their contents of K,Ca,Mg, and Na, *J. Am. Soc. Agron.*, **36**, 608-614.
4. BURSTROM, H., 1934, Über antagonistische bei der Kationenaufnahme des Hafers, *Svensk Bot. Tidskr.*, **28**, 157-263.
5. EFFMERT, B., 1960, Über das Natrium als Pflanzennährstoff, untersucht an Speisemöhren, Sommerweizen und Ackerbohnen, *Z. Pfl. Ernähr. Düng.*, **89**, 201-211.
6. HEIMANN, H., 1959, Irrigation with saline water and the ionic environment, *Potassium Symp.*, **1958**, 173-220.
7. HUFFAKER, R.C. AND WALLACE, A., 1959, Sodium absorption by different plant species at different potassium levels, *Soil Sci.*, **87**, 130-134.
8. HUFFAKER, R.C. AND WALLACE, A., 1959, Effect of potassium and sodium levels on sodium distribution in some plant species, *Soil Sci.*, **88**, 80-82.
9. VAN ITALLIE, TH.B., 1948, Cation equilibria in plants in relation to the soil (II), *Soil Sci.*, **65**, 393-416.
10. KOHL, H.C., KOFRANEK, A.M. AND LUNT, O.R., 1956, Effects of various ions and total salt concentration on *Saintpaulia*, *Am. Soc. Horticult. Sci.*, **68**, 545-550.
11. LARSON, W.E. AND PIERRE, W.H., 1953, Interaction of sodium and potassium on yield and cation composition of selected crops, *Soil Sci.*, **76**, 51-64.
12. LUNT, O.R. AND NELSON, W.L., 1950, Studies on the value of sodium in the mineral nutrition of cotton, *Proc. Soil Sci. Soc. Amer.*, **15**, 195-200.
13. REIFENBERG, A. AND ROSOVSKY, R., 1947, Saline irrigation water and its effect on the intake of ions by barley seedlings, *Palestine J. Rot.*, Ser. **4**, 1-13, Jerusalem.
14. REITEMEIER, R.F., 1957, Soil potassium and fertility, *USDA Year-Book of Agriculture*, 1957, 101-106.
15. SANKARANARAYANAN, M.P. AND VERGHESE, E.J., 1959, Role of sodium as a plant nutrient and substitute for potassium, *Indian Coconut*, **12**, 35-45.
16. SCHARRER, K. AND MENGE, K., 1960, Aufnahme und Verteilung der Kationen Ca, Mg, K und Na in der Pflanze bei variiert K- und Mg-Düngung sowie bei extraradikaler K-Versorgung, *Plant and Soil*, **12**, 377-396.

SOLVATION NUMBERS OF IONS FROM COMPRESSIBILITIES

J. PADOVA

Israel Atomic Energy Commission Laboratories

ABSTRACT

The hydration numbers of ions at infinite solution were computed from published compressibility data.

It can in general be written about solutions at infinite dilution that:

$$\varphi_s^\circ = \varphi_r^\circ + n^\circ V^\circ \quad (1)$$

where φ_s° is the molar volume of the solvated solute, φ_v° the apparent molar volume of the solute, n° the solvation number and V° the molar volume of the pure solvent. Differentiating this equation with respect to pressure P at constant temperature T gives

$$\left(\frac{\partial \varphi_s^\circ}{\partial P}_T\right) = \left(\frac{\partial \varphi_v^\circ}{\partial P}_T\right) + n^\circ \left(\frac{\partial V^\circ}{\partial P}_T\right) + V^\circ \left(\frac{\partial n^\circ}{\partial P}_T\right) \quad (2)$$

or following the definitions $\left(\frac{\partial \varphi_v^\circ}{\partial P}_T\right) = -\varphi_k^\circ$, $- \frac{1}{V^\circ} \left(\frac{\partial V^\circ}{\partial P}_T\right) = \beta^\circ$

$$\left(\frac{\partial \varphi_s^\circ}{\partial P}_T\right) = -\varphi_k^\circ - \beta^\circ V^\circ n^\circ + V^\circ \left(\frac{\partial n^\circ}{\partial P}_T\right) \quad (3)$$

It is now assumed that the solvation layer has negligible compressibility, from which follows that the differentials in equation (3) vanish. Hence:

$$n^\circ = -\frac{\varphi_k^\circ}{\beta^\circ V^\circ} \quad (4)$$

Equation (4) may be regarded as a shortcut to Passynsky's calculations¹ of primary solvation numbers from measurements of the compressibility of solvent and of solutions of electrolytes.

This relation can be checked with the help of very accurate results obtained by Kronick². Using $V^\circ = 18.06 \text{ cm}^3$ and $\beta^\circ = 4.524 \times 10^{-5} \text{ bar}^{-1}$, the values in Table

I are obtained, and are compared with those cited by Conway³. The agreement is rather good.

TABLE I

	NaCl	NaBr	KCl	KBr
$-10^4 \phi_k^\circ$	46.7	39.2	40.2	32.9
n°	5.7	4.8	4.8	4.0
average values (Conway ⁽³⁾)	6 ± 2	6 ± 2	5 ± 3	5 ± 3

The advantage of this method lies in the additivity of ϕ_k° for the various ions. Owen and Birnkley's⁴ results on the compressibility of solutions show that NH₄I and NH₄CNS have small positive compressibilities which may be due to these three ions being unhydrated.

Their ionic solvation numbers thus are zero. The ionic hydration numbers of other ions were computed from these results⁴, and are shown in Table II.

TABLE II

Cations	n°	Anions	n°
Li ⁺	2	OH ⁻	8
Na ⁺	3	Cl ⁻	3
K ⁺	2	Br ⁻	2
Cs ⁺	1	I ⁻	0
NH ₄ ⁺	0	CH ₃ COO ⁻	4
Mg ⁺⁺	8	NO ₃ ⁻	1
Ca ⁺⁺	8	CNS ⁻	0
Ba ⁺⁺	8	HCO ₃ ⁻⁻	2
Cd ⁺⁺	5	CrO ₄ ⁻⁻	13
Cu ⁺⁺	5	CO ₃ ⁻⁻	15
Zn ⁺⁺	6	SO ₄ ⁻⁻	11
Be ⁺⁺	1		
Ce ⁺⁺⁺⁺	13		

The figures obtained seem quite reasonable: and justify the approximations involved in deriving equation (4).

The number obtained for Li is lower than expected but the same result is mentioned (cf. ref. 3, p. 68) where it has been derived by a different calculation.

REFERENCES

- PASSYNSKY, A., 1938, *Acta Physicochimica*, **8**, 835.
Kronick — Dissertation Yale University 1957, loc cit. by HARNED, H.S. AND OWEN, B.B., *The Physical Chemistry of Electrolytes*, 3rd edition, p. 389. See also OWEN, B.B. AND SIMONS, H.L., 1957, *J. Phys. Chem.*, **61**, 479.
- CONWAY, B., *Ionic Solvation*, from Modern Aspects of Electrochemistry by I.O.M. BOCKRIS.
- OWEN, B.B. AND BRINKLEY, S.R., 1941, *Chem. Rev.*, **29**, 461.

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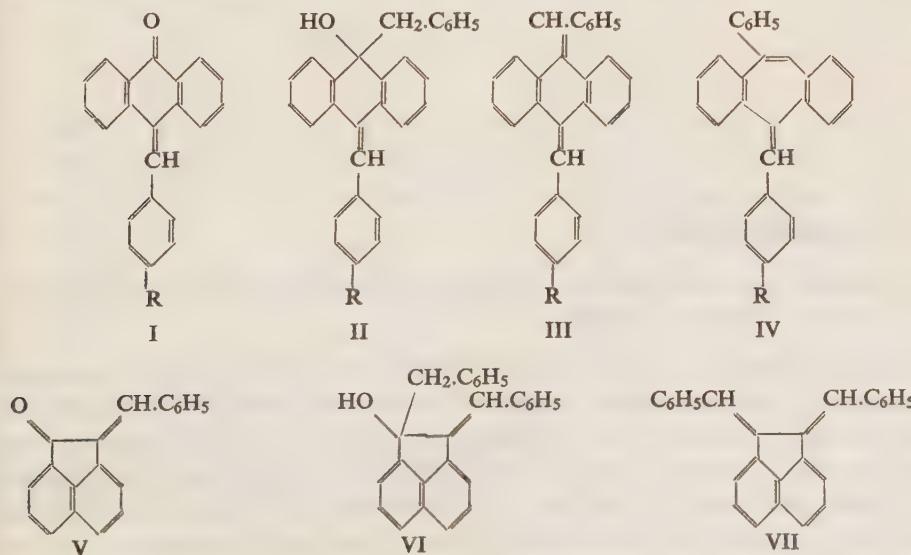
Ring enlargements in the polycyclic series

ERNST D. BERGMANN AND MORDECHAI RABINOWITZ, *Department of Organic Chemistry, The Hebrew University of Jerusalem*

It was found that benzoylideneanthrone (I, R=H) and *p*-chloro-benzylidene-anthrone (I, R=Cl) react with benzylmagnesium chloride by 1,2-addition (and not, as has been presumed before, by 1,6-addition). (II, R=H), m.p.) 125–127°, and (II, R=Cl), m.p. 193–194°, are formed, respectively. Dehydration of the alcohols (II) with acetic anhydride proceeds “normally”, leading to the known 9,10-dibenzylidene-9,10-dihydroanthracene (III, R=H), m.p. 203–204°, and its *p*-chloro-derivative (III, R=Cl), m.p. 199–200°, respectively. If the dehydration is carried out with boiling formic acid, ring enlargement takes place, giving the derivatives (IV) of dibenzocycloheptatriene: IV, R=H, m.p. 145–147°; IV, R=Cl, m.p. 167–168°.

Analogously, benzylidene-acenaphthenone (V) gives a “normal” reaction product (VI, m.p. 179°) with benzylmagnesium chloride. Its dehydration with acetic anhydride leads to the known dibenzylideneacenaphthene (VII), whilst with formic acid an isomeric hydrocarbon is formed.

The proof for the structure of these substances and the mechanism of their formation will be discussed.



Contribution to the theory of thermochromic ethylenes

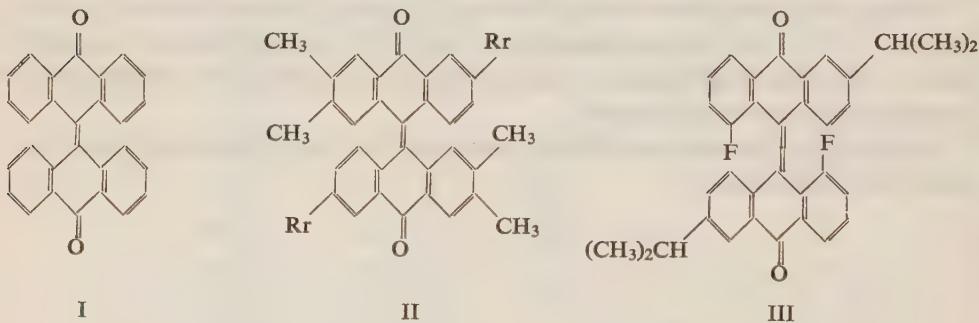
ERNST BERGMANN AND ADAM HELLER, *Department of Organic Chemistry, The Hebrew University of Jerusalem*

With the aid of the LCAO method (linear combination of atomic orbitals), the configuration of bianthrone (I) has been calculated, which is a thermochromic, photochromic and piezochromic compound. Two opposing factors determine the configuration of the molecule: the tendency to minimize the electronic energy by increasing the degree of planarity, and the interatomic repulsion of the four ortho-hydrogen atoms which causes a twist.

The sum of the two energies was found to have *two* minima, corresponding to the colourless and the coloured forms. The ground state is more twisted, the excited (coloured) state more planar.

As this is not the accepted theory, the dipole moments of the two new bianthrone (II) and (III) were determined ($4.3 \pm 1.0D$; $2.26 \pm 0.14D$) in the ground state. The ground state is, indeed, far from planarity.

The synthesis and other properties of (II) and (III) will be discussed.



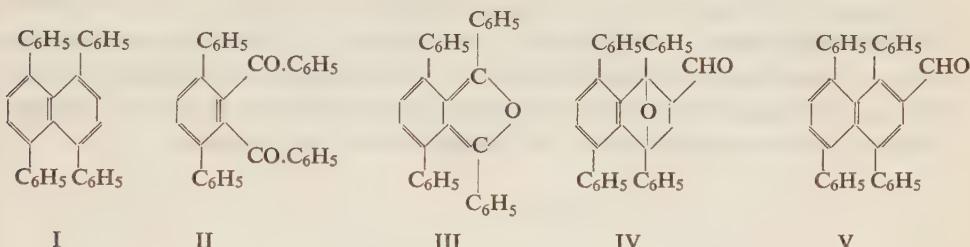
1,4,5,8-tetraphenylnaphthalene

ERNST BERGMANN AND SHMARYAHU BLUMBERG, *Department of Organic Chemistry, The Hebrew University of Jerusalem*

Recently, the influence of the substitution, by alkyl and aryl groups, on the aromatic character of the naphthalene system has been studied extensively. Of particular interest seemed to be the 1,4,5,8-tetraphenyl derivative (I) of naphthalene, in view of the unusual properties of rubrene (9,10,11,12-tetraphenylnaphthacene) and 1,4,9,10-tetraphenylanthracene. (I) has been synthesized through the steps II, III, IV and V, II being available by diene synthesis from 1,4-diphenylbutadiene and *trans*-1,2-dibenzoylethylene and subsequent dehydrogenation.

(I) has a completely featureless ultraviolet spectrum and is, thus, probably not planar. It exhibits a distinct (violet-blue) fluorescence; acid does not isomerize it.

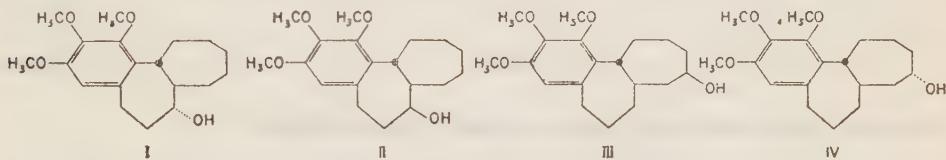
Some other experiments on the synthesis of phenylated naphthalenes will also be reported.



Structural and conformational aspects in fused seven membered ring systems

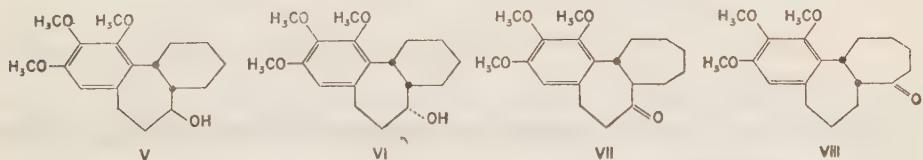
H.J.E. LOEWENTHAL AND P. RONA*, Technion-Israel Institute of Technology, Haifa

The stereospecific reactions^{1,2} and the relative reactivity of the alcohols (I), (II), (III), (IV) and (VI) and the corresponding acetates shows that it is possible



to apply conformational analysis to fused seven membered ring systems.

Basic epimerization of the ketones VII and VIII shows a preferential thermodynamic stability in the case of *trans* fusion between two seven membered rings.



REFERENCES

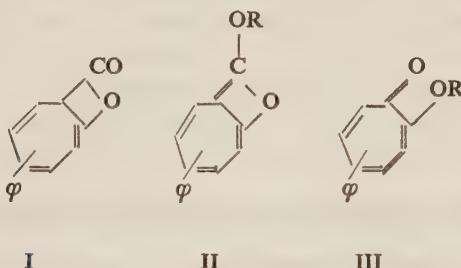
1. LOEWENTHAL, H.J.E., 1958, *J. Chem. Soc.*, 1367.
2. LOEWENTHAL, H.J.E. AND RONA, P., 1958, *Proc. Chem. Soc.*, 114.

* Lecturer

The formation and properties of β -lactone of phenyl 2-hydroxycycloheptatriene carboxylic acid

ELI BREUER* AND SHALOM SAREL, *Department of Pharmaceutical Chemistry, The Hebrew University of Jerusalem*

In a study aimed at investigating the cyclo-addition reaction of maleic anhydride to α -cyclopropylstyrene, a new β -lactone was isolated¹, to which formula I has been assigned. The present communication reports the ready transformation of I either into a new hetero-azulene (II) or to a tropolone system (III). Chemical and physical evidence corroborating the structural assignments will be presented.

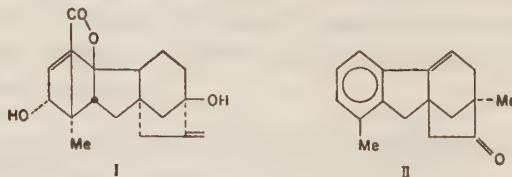


REFERENCES

.1 SAREL, S. AND BREUER, E., 1959, *J. Amer. Chem. Soc.*, **81**, 6522.

Synthetic approaches to compounds related to gibberellic acid

E. LOEWENTHAL* AND N. MAOZ, *Technion-Israel Institute of Technology, Haifa*

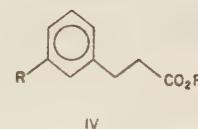
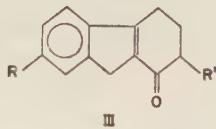


In connection with a synthetic programme related to gibberellic acid (I), the following will be described:

(a) A number of novel approaches towards the construction of the bicyclo [3,2,1] octane system as present in (I).

* Lecturer

(b) A total synthesis of gibberone (II), a degradation product of (I), in hitherto unpublished detail, including some aspects of stereo-specific reactions.
 (c) A novel and short synthesis of derivatives of 1,2,3,4-tetrahydrofluoren-4-one (III), which starts from m-substituted phenylpropionic acids (IV).



Session OB — Tuesday 4.4.61, 11.45–13.00

Chairman: E. D. BERGMANN

Synthesis of new steroidal systems

YEHUDA MAZUR, *The Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth*

A three step conversion of $\Delta^{1,9}$ decalins (I) into perhydro-azulenes (II) was developed. This conversion involves a novel stereospecific rearrangement of bicyclo [4:4:0]-decane-cis-1,9-diol 1-tosylate to bicyclo [5:3:0] decane 4-one. This reaction was applied in the steroids and new steroidal systems were synthesized. Those include A-Homo, B-Nor and B-Homo, A-Nor cholestans and coprostans. The relative stability of cis- and trans- bicyclo [5:3:0]-decan-4-ones will be discussed.



Synthesis of purines substituted at carbon 8

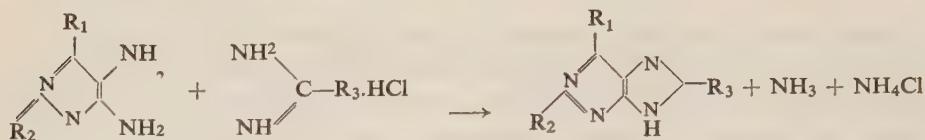
MEIR TAMARI* AND FELIX BERGMANN, *Department of Pharmacology, The Hebrew University-Hadassah Medical School, Jerusalem*

The introduction of substituents into position 8 of the purine ring has been achieved previously by acylation of the 5-amino group in 4,5-diaminopyrimidines, followed

* Lecturer

by cyclisation^{1,2,3}. This method requires very drastic conditions and gives unreliable results.

Condensation can be achieved in a much simpler way and with good to excellent yields, by eliminating NH₃ instead of H₂O according to



where R₃ = methyl or phenyl.

The compounds obtained according to this method are represented in Table I. The mechanism of the condensation reaction will be discussed.

TABLE I
Properties of 8-substituted purines.

R ₁	R ₂	R ₃	Yield %	λ_{max} at pH 8	A	R _F	B
OH	H	CH ₃	56	252	0.57	0.70	
OH	OH	CH ₃	94	240 275	0.54	0.60	
SH	OH	CH ₃	83	251 344	0.50	0.56	
OH	SH	CH ₃	77	235 280	0.45	0.74	
SH	SH	CH ₃	95	247 285 351	0.53	0.59	
NH ₂	SH	CH ₃	66	230 251 280	0.61	0.67	
OH	H	C ₆ H ₅	50	291	0.58	0.79	
OH	OH	C ₆ H ₅	80	228 309	0.52	0.66	

Solvent A: Ethanol, 95% — 85 vols.; water — 10 vols.; glacial acetic acid — 5 vols.

Solvent B: Ethanol, 95% — 70 vols.; pyridine — 20 vols.; water — 10 vols.

REFERENCES

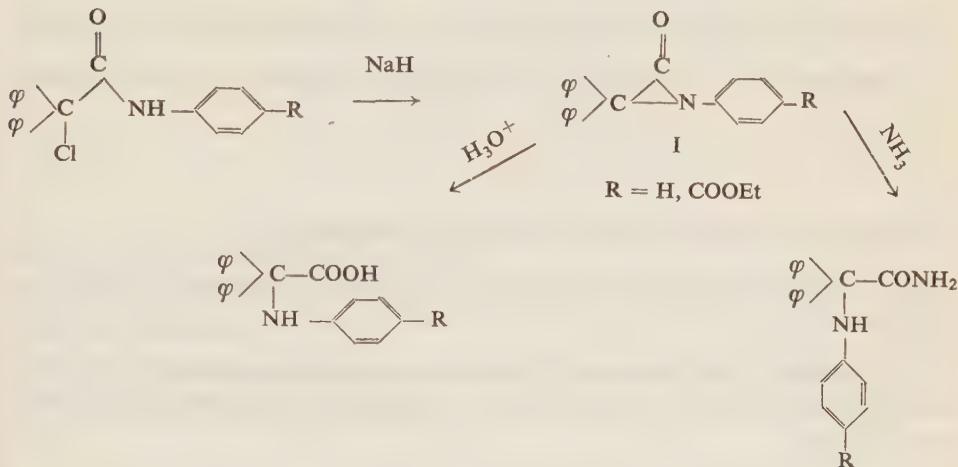
- ISAY, O., 1906, Ber. **39**, 250.
- ALBERT, A. AND BROWN, D. C., 1954, J. Chem. Soc., 4935.
- KOPPEL, H. C. AND ROBINS, R. K., 1958, J. Org. Chem., **23**, 1457.

The synthesis and properties of arylated α -lactams

SHALOM SAREL* AND HAIM LEADER, Department of Pharmaceutical Chemistry, The Hebrew University of Jerusalem

The present communication reports the synthesis of a new class of compounds, α -lactams, by the action of sodium hydride on phenylated α -chloroacetanilide.

Structural assignments of products presented here were based upon both spectroscopic

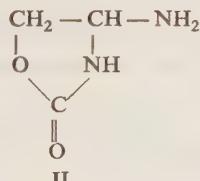
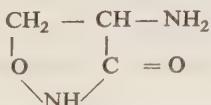


pic and chemical evidence. The reactivity of the amide function is largely affected by the number and the nature of aryl groups. Nucleophilic displacements involve carbonyl-nitrogen bond-fission, providing α -anilino-acid derivatives, as described in the chart. The synthetical and theoretical aspects of this reaction will be discussed.

4-amino-2-oxazolidinones

J. STRUMZA AND D. BEN-ISHAI*, Technion-Israel Institute of Technology, Haifa

Cycloserine (oxamycin) a natural occurring antibiotic is an isooxazole derivative (I)



* Lecturer

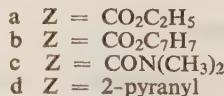
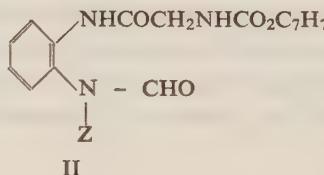
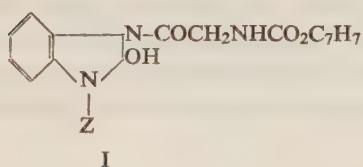
In the present work a number of 2-oxazolidinone derivations structurally related to the antibiotic were synthesized:

1. The isomeric 4-amino-2-oxazolidinone (II) and four of its acyl derivatives (*N*-benzoyl, *N*-phenylacetyl, *N*-carbethoxy and *N*-carbobutoxy).
2. Two methyl derivatives: 5-methyl-4-amino-2-oxazolidinone 5, 5-dimethyl-4-amino-2-oxazolidinone and their acyl derivatives (*N*-benzoyl, *N*-phenylacetyl, *N*-carbethoxy and *N*-carbobutoxy).
3. 2-Oxazolidinones having carboxyl or alkoxy functional groups in the 4 position.
4. In addition, two 2-oxazolidones and a dimeric derivative of II were obtained.

The reactions of carbobenzoxyglycylchloride with benzimidazoles

JANINA ALTMAN* AND DOV BEN-ISHAI, *Technion-Israel Institute of Technology, Haifa*

The reaction of carbobenzoxyglycylchloride with nitrogen-substituted benzimidazoles, under Schotten-Baumann reaction conditions, affords two types of products (I, II):



Compound IIa looses its formyl group easily whereas the deformylation of IIb and IIc is achieved only after treatment with ammonia. The position of the formyl group in IIb has been proved by catalytic hydrogenation and recarbobenzoylation.

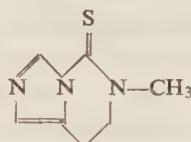
Under pyrolytic conditions the compounds of type II cyclize to form 2-benzimidazolone derivatives.

* Lecturer

The structure of zapotidine

R. MECHOULAM AND F. SONDHEIMER, *The Weizmann Institute of Science, Rehovoth*

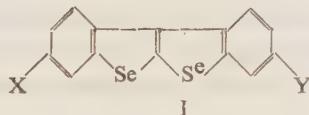
The alkaloid zapotidine, a constituent of the seed of the tree *Casimiroa edulis* Llave et Lex., has been shown to possess the unusual structure shown below. This type of ring system has not been encountered previously in a natural product, and it is moreover exceedingly rare for a thiourea derivative to occur in nature.



Reaction of SeOCl₂ with diaryl ethylenes

S. PATAI AND A.K. MUSZKAT, *Department of Organic Chemistry, The Hebrew University of Jerusalem*

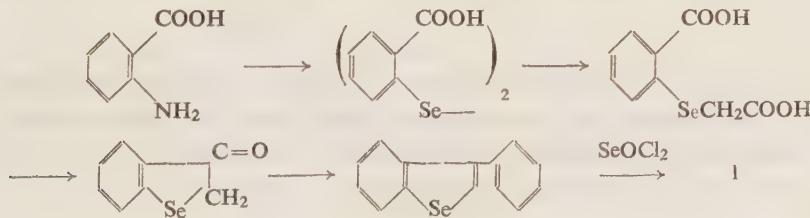
Since the publication of a preliminary notice on the reaction of SeOCl₂ with diaryl ethylenes¹ a series of new selenonaphtheno (2,3-b) selenonaphthenes



derivatives have been synthesised, where X=Y=CH₃O, (CH₃)₃C-; X=H, Y=C₆H₁₁.

Moreover, di- β -naphthylethylene, α,β -dinaphthylethylene and phenylnaphthylethylenes also underwent the reaction.

The structure of the parent compound (I, X=Y=H) has been proved by a new independent synthesis including the following main steps:



Steric effects on the reaction between substituted diarylethylenes and SeOCl₂ will be discussed, as well as the steric requirements for electrophilic aromatic substitution in I.

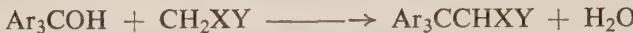
REFERENCES

1. 1960, *Proc. Chem. Soc.*, 181.

C-tritylations of aliphatic compounds*

SHLOMO DAYAGI AND SAUL PATAI, *Department of Organic Chemistry, The Hebrew University of Jerusalem*

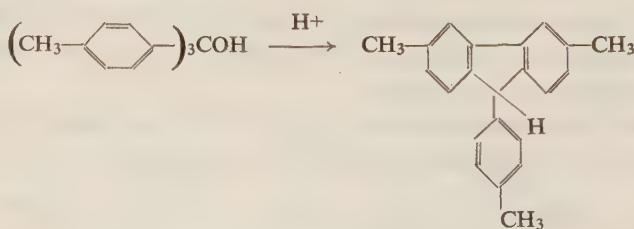
Triarylcarbinols react with active methylene compounds according to the scheme



when X and Y are strongly electron-attracting groups. The reaction is carried out under conditions favourable to the formation of the Ar_3C^+ carbonium ions from the corresponding carbinols. Triphenylcarbinol, for example, reacts with weakly acidic active methylene compounds in acidic media, such as in the presence of H_2SO_2 (with malondiamide) or CCl_3COOH (H_2SO_4), at temperatures between room temperature and 100°C. For more acidic active methylene compounds such as malonic acid, cyanoacetic acid¹ and even malononitrile, the reaction can be carried out by heating the two reactants above their melting points, giving better yields.

The reaction with nitriles is complicated, since the addition of the carbinol to the cyano group may give substituted amides of the type $-\text{CONHCAr}_3$.² The relative amounts of the condensate and the adduct depend upon the reaction conditions, acidity and temperature.

The number of carbinols subject to the condensation is limited. Carbinols (e.g., nitro substituted triarylcarbinols), which have a low tendency to give the corresponding carbonium ions, do not condense with methylene compounds. On the other hand, triarylcarbinols of enhanced reactivity (e.g., tri-*p*-tolylcarbinol), also fail to react, or give low yields, probably owing to preferential intramolecular cyclization reactions.



Contrary to most of the reactions of active methylene compounds, which proceed through initial formation of the *carbanions* CHXY , and are base-catalyzed, this reaction shows only acid catalysis, and the governing step seems to be the carbonium ion formation and its attack upon the methylene compound.

REFERENCES

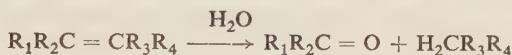
1. FOSSE, R., 1907, *Compt. Rend.*, **145**, 196-8.
2. FOSSE, R., 1931, *Bull. Soc. Chim. France*, **4**, 49, 159-73.

* Taken in part from a Ph. D. thesis of S. Dayagi

The mechanism of hydrolysis of activated carbon-carbon double bonds in 95% ethanol*

Z. RAPPOPORT AND S. PATAI, *Department of Organic Chemistry, The Hebrew University of Jerusalem*

It was shown in a number of cases that compounds containing carbon-carbon double bonds, activated by electron-attracting substituents are cleaved by water without a catalyst according to the equation^{1,2}

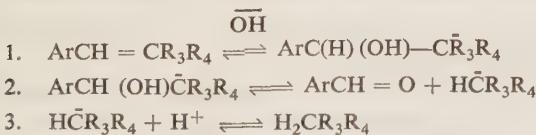


We investigated the kinetics of this cleavage reaction in 95% ethanol when $\text{R}_1=\text{H}$, $\text{R}_2=\text{substituted benzene ring}$, $\text{R}_3=\text{CN}$ and $\text{R}_4=\text{CN}$, COOEt , CONH_2 at 30° and 40° by a spectrophotometric method.

It was found that the rate of hydrolysis is increased by introducing electron-attracting substituents (the ratio $p\text{-CH}_3\text{O}-$ to $p\text{-NO}_2-$ being 1:800 when $\text{R}_4=\text{CN}$), and by varying R_4 according to the order $\text{CN} > \text{COOEt} > \text{CONH}_2$ (40:4:1, when $\text{R}_2=p\text{-CH}_3\text{OC}_6\text{H}_4-$).

The effect on the rate of added base, acid and salt was studied. It was shown that addition of base increases the rate, while addition of small quantities of acids retarded the rate greatly. Addition of salts has only small effects. The rate of the reaction increases with the percentage of water in the alcohol from 0% to 50% (by volume).

From these results we propose the following mechanism for the reaction. The first step is a nucleophilic attack on the double bond by hydroxide ion or water, followed by a cleavage of the intermediate anion to aldehyde and the anion of the active methylene compound, according to the scheme:



REFERENCES

1. SHEMYAKIN, M. M. AND SHCHUKINA, L. A., 1956, *Quart. Rev.*, **10**, 261, (and references quoted therein).
2. ZABICKY, J., Personnal communication.

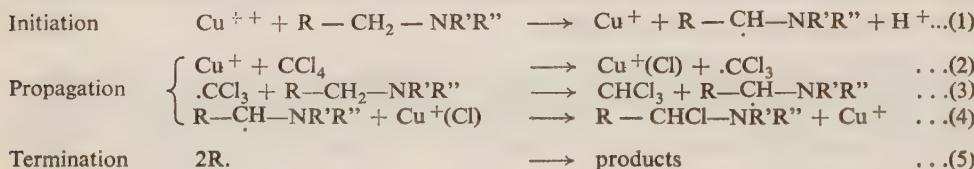
* Taken in part from the Ph. D. thesis of Z. Rappoport

The reaction between aliphatic amine and carbon tetrachloride (chlorine activation by redox-transfer)

M. ASSCHER AND D. VOFSI, *Plastics Research Laboratory, Polymer Department, The Weizmann Institute of Science, Rehovoth*

The reaction between amine and carbon tetrachloride gives 0.5 mole amine-hydrochloride on one mole amine, and is strongly catalyzed by copper and iron chlorides¹.

A free-radical chain mechanism is proposed² in which copper or iron ions participate in the initiation as well as in the propagation steps, thus:



The α -chloramine formed in (4) is a precursor of amine hydrochloride. The following observations support the above chain mechanism:

- The reaction has a well-defined induction period which can be eliminated by the addition of a soluble hydrochloride.
- Styrene strongly inhibits the reaction.
- The reaction induces the addition of carbon tetrachloride to olefines, which is a free-radical chain reaction³.

Step (4) is an established chain-breaking reaction^{4,5} but if followed by (2)—which is fast at room temperature⁶—a facile chain-transfer is obtained (“redox-transfer”).

In systems which permit redox-transfer, the apparent reactivity of carbon tetrachloride surpasses that of bromotrichloromethane.

Redox-transfer will in principle be possible only for compounds with positive halogen; otherwise the vital step (2) is impossible or even reversed.

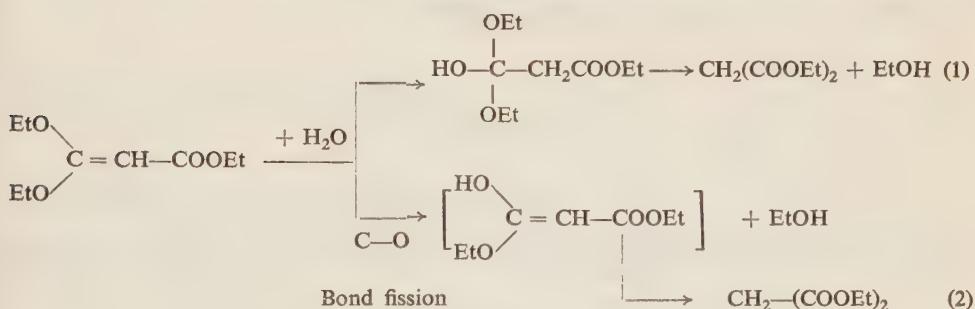
REFERENCES

- FOSTER ET AL., 1959, *Chem. and Ind.*, 228.
- ASSCHER AND VOFSI, *J. Chem. Soc.*, in press.
- KHARASH, JENSEN AND URRY, 1947, *J. Am. Chem. Soc.*, **69**, 1100.
- KUMAMOTO, DE LA MARE AND RUST, 1960, *ibid.*, **82**, 1935.
- KOCHI, 1956, *ibid.*, **78**, 4815.
- DOUGHTY, 1919, *ibid.*, **41**, 1131.

The mechanism of hydrolysis of carbethoxy keten acetal: Tracer studies

SHALOM SAREL*, ELI BREUER AND JACOB S. MENAHEM, *Department of Pharmaceutical Chemistry, The Hebrew University of Jerusalem*

The hydrolysis of ethyl $\beta\beta$ -diethoxyacrylate, whether in neutral or in acid media, occurs readily, providing diethyl malonate in quantitative yield. This reaction can conceivably be depicted as pursuing a mechanism either of the type (1) or that of (2).



The neutral and acid-catalysed hydrolysis of ethyl $\beta\beta$ -diethoxyacrylate in H_2^{180}O was undertaken in the hope of uncovering the type of mechanism occurring in this reaction. Our tracer studies show that the hydrolysis of the carbethoxy keten acetal may proceed by both types of mechanisms, depending on the acidity of the medium. In a neutral solution, the reaction is slow, involving the addition of water to the double-bond, by way illustrated in process (1). However, the hydrolysis in acid occurs rapidly, involving an alkyl-oxygen bond-fission, as depicted by route (2).

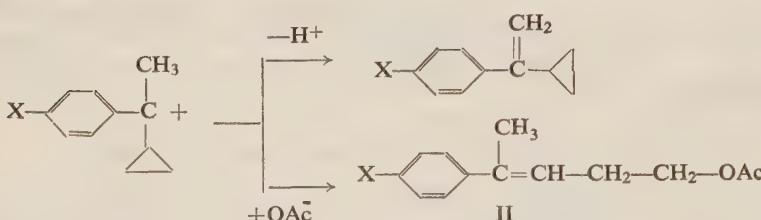
The stability of α -cyclopropylbenzylium ions as a controlling factor in their homoallylic rearrangement

SHALOM SAREL, ELI BREUER* AND SHULAMITH ERTAG, *Department of Pharmaceutical Chemistry, The Hebrew University of Jerusalem*

Dehydration of phenylcyclopropylmethyl carbinol by means of acetic-anhydride leads to the formation of a mixture composed of α -cyclopropylstyrene (I) and 4-phenyl α -pent-3-en-1-ol acetate (II) in a ratio 2:1. This observation was interpreted in terms of the formation at first of a cyclopropylbenzylium ion, which can then lead to the formation of stable products, either by a) β -elimination of a proton, providing I, or b) by homoallylic rearrangement¹, affording II². This study was undertaken in the hope of uncovering the effect of substitution in the para position of

* Lecturer

the phenyl group on the ratio I/II. If this ratio was to be affected by the stability of the intermediate carbonium ion³, then the yields of I and II would be expected to vary with the polar effects of substituents. Whereas, electron-attracting groups might increase yields of I, an increase in the yield of II would be expected by the influence of electron releasing substituents. Our results fully substantiate this postulate. Thus, higher yields of I being obtained in case of halogen substitution, and in case of methoxy-substituent, higher yields of II were obtained. The results obtained in a study of the catalytic hydrogenation of substituted phenylcyclopropyl ketones are in keeping with the above mechanistic pattern.



REFERENCES

1. WINSTEIN, S. AND KOSOWER, M., 1959, *J. Amer. Chem. Soc.*, **81**, 4399.
2. BREUER, E., 1961, Dissertation.
3. BROWN, H.C. AND OKAMOTO, Y., 1957, *J. Amer. Chem. Soc.*, **79**, 1913,

Sodium catalyzed equilibrium isomerization of cyclo-olefins

J. HERLING* AND E. GIL-AV, *The Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth*

Cyclo-olefins with a four-to six-membered ring and a one-carbon side chain were subjected to equilibrium isomerization over finely dispersed sodium on alumina¹ at 25°C. The reaction was rapid and proceeded without the formation of side products.

For the five and six-membered ring compounds the following equilibrium concentrations were found: Methylenecyclopentane 0.09%, 1-methylcyclopentene 97.6%, 3-methylcyclopentene 1.65% and 4-methylcyclopentene 0.67%; methylenecyclohexane 0.4%, 1-methylcyclohexene 91.0%, 3-methylcyclohexene 3.14% and 4-methylcyclohexene 5.45%. The ratios of exo/endo isomer in these series were the same as determined in acetic acid solution in the presence of *p*-toluene-sulfonic acid². This result shows that solvation by acetic acid does not practically effect the equilibrium position. Sodium on alumina, contrary to *p*-toluenesulfonic acid, catalyzes, already at room temperature, the migration of the double bond to all possible positions in the ring.

* Lecturer

In the four-membered ring series the equilibrium concentration of the exo isomer reaches 15%. This relatively very high value is ascribed to a decrease of the stability of the endo isomer by ring strain.

REFERENCES

1. *High Surface Sodium on Inert Solids*, U.S. Industrial Chemicals Co., New York, N.Y.
2. COPE, A. C., AINBROS, D., CIGANEK, E., HOWELL, F. AND YACURA, Z., 1959, *J. Amer. Chem. Soc.*, **82**, 1750.

Session O_E — Tuesday 4.4.61, 17.00–18.00

Chairman: J. LIWSCHITZ

The reaction of oxalofluoroacetate with aldehydes

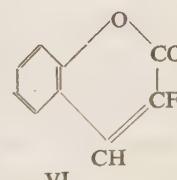
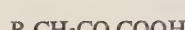
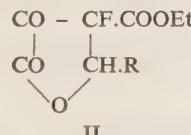
ERNST BERGMANN AND ISRAEL SHAHAK, Department of Organic Chemistry, The Hebrew University of Jerusalem

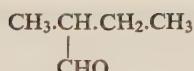
The condensation of aldehydes RCHO with diethyl oxalofluoroacetate can lead, according to conditions, to compounds of the types I, II and III, the most interesting amongst them being the substituted α -fluoroacrylic acids (III); their constitution follows from their hydrolysis to substituted α -ketoacids (IV).

Phenylacetaldehyde gives a β , γ -unsaturated acid (V), *O*-acetoxybenzaldehyde fluorocoumarin (VI) (in two steps).

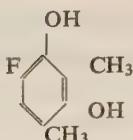
As ketones do not react with oxalofluoroacetate, the ketoaldehyde (VII) was studied; it was converted into 2,4-dimethyl-6-fluororesorcinol (VIII).

Analogously α -ethoxalyl-derivatives of aliphatic or arylaliphatic esters (IX) can be converted into α,β -dialkylated acrylic acids (X) by condensation with aldehydes R'CHO.

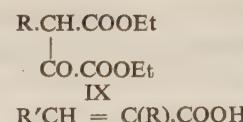




VII



VIII



x

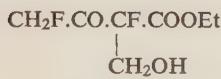
α -fluoro- β -alanine and α -fluoroglutamic acid

ERNST D. BERGMANN AND SASSON COHEN, *Israel Institute for Biological Research, Ness-Ziona*

Fluoro-substituted amino-acids are likely to act as antimetabolites of the parent compounds, a fact which had been well established in the series of *aromatic* amino-acids.

For the synthesis of α -fluoro- β -alanine, the hydroxymethylation of suitable α -fluoro esters has been studied, which has been carried out with success in the case of diethyl oxalofluoroacetate.

Ethyl α,γ -difluoroacetoacetate, ethyl γ,γ -dichloro- α -fluoroacetoacetate and diethyl fluoromalonate were easily converted, by means of formaldehyde, into the compounds (I), (II), (III). The methanesulphonate of (III) gave with potassium-phthalimide compound (IV) from which α -fluoro- β -alanine (V) was prepared in the conventional manner.



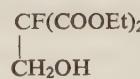
$$\text{CH}_2\text{OH}$$

$$\text{CHCl}_2.\text{CO}.\text{CF}.\text{COOEt}$$

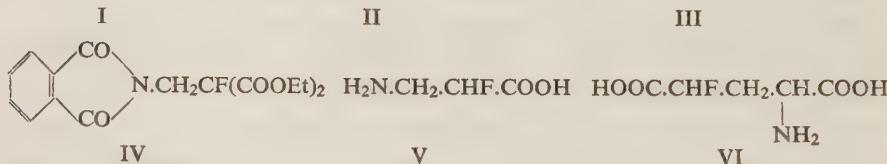
|

$$\text{CH}_2\text{OH}$$

$$\text{CH}_2\text{OH}$$



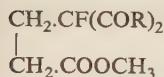
$$\text{CH}_2\text{OH}$$



One synthesis of α -fluoroglutamic acid (VI) has recently been described by Hudlicky¹, who essentially carried out a Michael condensation of diethyl aceta-midomalonate and ethyl α -fluoro-acrylate.

We have tried the synthesis of (VI) by condensing diethyl fluoromalonate or fluoromalondiamide with methyl acrylate and hydrolysing the product (VII).

$R = OEt$ or NH_2) to α -fluoroglutamic acid (VIII). α -Bromo- α -fluorglutaric acid (IX), was then treated with methanolic ammonia.



VII



VIII



IX

REFERENCE

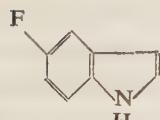
1. HUDLICKY, M., 1960, *Tetrahedron Letters*, No. 14, 21.

5 γ **fluoroindole and some of its derivatives**

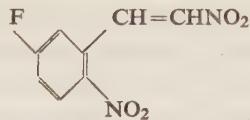
ASHER KALUSZYNER AND M. BENTOV, *Israel Institute for Biological Research, Ness-Ziona*

Two methods have been applied with success to the synthesis of 5-fluoroindole (I): The reductive cyclisation of 5-fluoro-2- ω -dinitro-styrene (II) and the transformation of 2-amino-5-fluorobenzoic acid (III) into 5-fluoro-3-hydroxyindole (IV).

From (I), the fluoro-analog of bufotenin as well as 5-fluorotryptophan have become easily available. Details of the syntheses and some pharmacological data will be discussed.



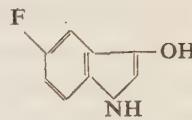
I



II



III



IV

Syntheses of fluorine-substituted polycyclic compounds

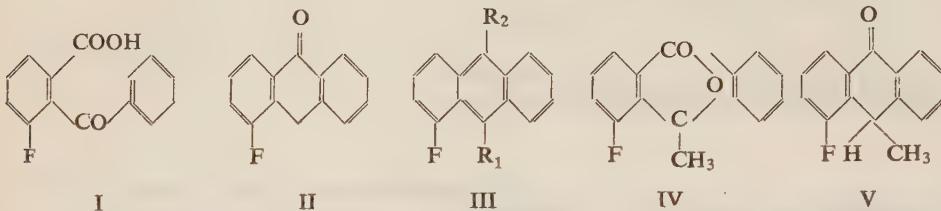
M. BENTOV AND ERNST D. BERGMANN, *Israel Institute for Biological Research, Ness-Ziona*

The easily available¹ 3-fluorophthalic anhydride gives with benzene only one of the theoretically possible two isomers, *viz.* 2-benzoyl-3-fluorobenzoic acid (I). This has been proven by reduction of (I) and subsequent cyclization to 1-fluoro-10-anthrone (II) which has been synthesized before by a different method.²

Grignard reaction of (II) with methylmagnesium bromide gives 1-fluoro-10-methylanthracene (III, $R_1=H$; $R_2=CH_3$). Interaction of (I) with methylmagnesium bromide produces the lactone (IV) which by reduction and cyclisation leads to 1-fluoro-9-methyl-10-anthrone (V). Reduction of this compound gives 1-fluoro-9-

methylanthracene (III, $R_1=CH_3$, $R_2=H$); reaction with methylmagnesium bromide 1-fluoro-9,10-dimethylanthracene (III, $R_1=R_2=CH_3$).

Details on the analogous preparation of other fluorine-substituted polycyclic compounds will be presented.



REFERENCES

1. HELLER, A., 1960, *J. Org. Chem.*, **25**, 834.
2. BERGMANN, E.D. AND ROJANSKI, C., private communication.

Session OF — Wednesday 5.4.61, 9.00–10.00.

Chairman: W. TAUB

O-dialkyl methylphosphothionates and O-alkyl-methyl-phosphothiolic acids

ZVI PELCHOWICZ*, Sasson COHEN AND HAIM LIDER, *Israel Institute of Biological Research, Ness-Ziona*

For the synthesis of these two groups of substances, which are of considerable interest for the preparation of insecticides, only very cumbersome methods have been available. The following new approaches have been developed: Reaction between methylthiophosphonyl dichloride and an alcohol in the presence of 0.5% boron trifluoride gives the O,O-dialkyl methylphosphothionate; only in the case of isopropanol, is the reaction product O-isopropyl-methyl phosphothiolic acid.

If the same reaction is carried out in the presence of potassium hydroxide (instead of boron trifluoride), the potassium salt of the O-alkyl-methylphosphothiolic acid is formed instantaneously. Again, in the case of isopropyl alcohol, the dipotassium salt of methylphosphothiolic acid is also formed.

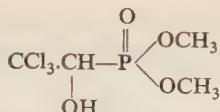
The reaction mechanisms involved will be discussed.

New compounds in the dipterex series

ZVI PELCHOWICZ*, *Israel Institute of Biological Research, Ness-Ziona*

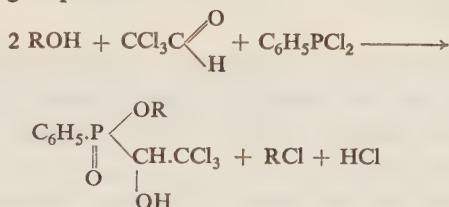
1. Modifications have been carried out in the molecule of dipterex (dimethyl 2,2,2-trichloro-hydroxyethylphosphonate)

* Lecturer



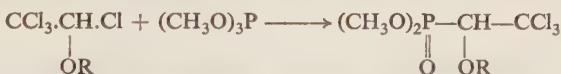
by exchanging one of the methoxy-groups by phenyl, the other by various alkoxy-groups.

The method elaborated for the synthesis of the desired substances is described by the following equation:



The reaction takes place smoothly and gives excellent yields; only in the case of *t*-butanol, the acid is obtained instead of the *t*-butyl ester (OH instead of OR).

2. From trimethyl phosphite and alkyl (1,2,2,2-tetrachloroethyl) ethers, ethers of dipterox are formed:



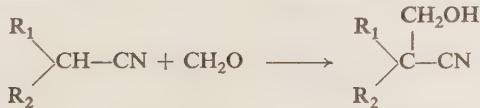
The lecture will also discuss the toxicological data concerning the new compounds and some theoretical conclusions derived from them.

A new synthesis of β -hydroxypropionitriles

M. AVRAMOFF* AND Y. SPRINZAK, *The Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth*

The reaction of active methylene compounds with carbonyl compounds in pyridine solution in the presence of Triton B₁ has been extended to acetonitrile derivatives and formaldehyde.

Treatment of disubstituted acetonitriles with paraformaldehyde affords α,α -disubstituted β -hydroxypropionitriles in yields ranging from 44% to 95%.



The presence of an α -aryl group is essential for the reaction to occur, as is indicated by the failure of dibenzylacetonitrile to react.

* Lecturer

Under basic conditions the β -hydroxynitriles are converted, by a reverse aldol reaction followed by hydrolysis, to the corresponding acetic acids.

REFERENCE

1. GHERA, E. AND SPRINZAK, Y., 1960, *J. Am. Chem. Soc.*, **82**, 4945.

Inter-reactions of D-fructose in organic solvents

A.H. SHAMGAR AND J. LEIBOWITZ, *Department of Biological Chemistry, The Hebrew University of Jerusalem*

The exceptional reactivity of the D-fructose molecule, which has been demonstrated by the results of treatment with acids^{1,2,3} has now been shown to find an even more drastic expression in inter-reactions with non-ionic organic solvents (ethanol and methanol) without any catalyst.

Heating D-fructose with ethanol produces a series of degradation, anhydridisation, polymerisation and condensation products, including methylglyoxal, difructopyranose and difructofuranose dianhydrides and β -ethylfructoside.

The difructose dianhydrides, β -methylfructopyranoside and other not yet identified substances were formed when methanol was used as solvent.

Within a week one third of the D-fructose was converted into the various non-reducing products.

No such conversions could be detected in case of D-glucose and D-mannose and also in the cases of the ketoses, sorbose, sedoheptulose and mannoheptulose.

REFERENCES

1. PICTET, A. AND CHAVAN, J., 1926, *Helv. Chim. Acta*, **9**, 809.
2. WOLFROM, M. L., BINKLEY, W. W. AND HILTON, H. W., 1952, *J. Am. Chem. Soc.*, **74**, 2867.
3. SHAMGAR, A. H. AND LEIBOWITZ, J., 1960, *J. Org. Chem.*, **25**, 430.

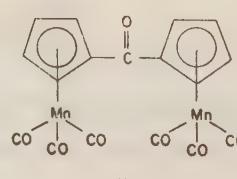
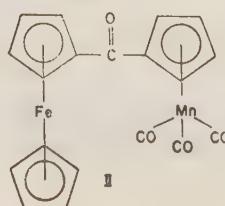
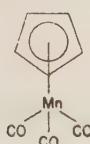
Session OG — Wednesday 5.4.61, 10.15–11.14

Chairman: J. LEIBOWICH

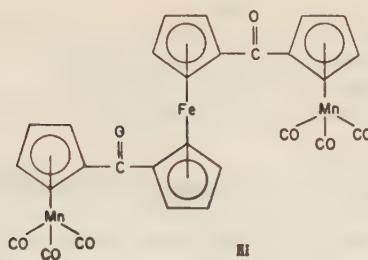
The syntheses of novel organometallic compounds

M. FELDKIMMEL AND MICHAEL CAIS*, Technion-Israel Institute of Technology, Haifa

The recently described¹ ferrocenyl ruthenocenyl ketone, prompts us to report the syntheses of the novel compounds II, III and IV obtained in our laboratories in the course of an investigation^{2,3} of the chemistry of cyclopentadienylmanganese tricarbonyl, I.



* Lecturer



Compound III represents the first reported derivative containing three metallocene moieties incorporated into a neutral compound.

The synthesis of the new compounds as well as some of their properties provides further evidence of the benzene-like properties⁴ of the cyclopentadienyl ring in I.

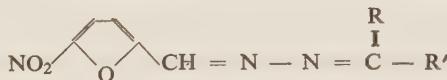
REFERENCES

- RAUSCH, M., FISCHER, E.O. AND GRUBERT, H., 1960, *J. Amer. Chem. Soc.*, **82**, 76.
- CAIS, M. AND MODIANO, A., 1960, *Chem. and Ind.*, 202.
- MODIANO, A. AND CAIS, M., 1960, *Tetrahedron Letters*, **18**, 31.
- CAIS, MICHAEL AND KOZIKOWSKI, JOHN, 1960, *J. Am. Chem. Soc.*, **82**, 5667.

Asymmetric nitrofurfural azines

R. G. HABER*, R. GURI AND E. MENACHEMOFF, *Technion-Israel Institute of Technology, Haifa and "Abic Ltd."*

Nitrofuran derivatives are known as antibacterial compounds^{1,2}. We prepared new derivatives of the general formula



in order to test their antibacterial and antifungal properties. The groups R and R' were hydrogen, methyl, various mono and disubstituted phenyls, pyridyl, furyl and naphthyl³. Assymmetric azines are mentioned sparingly in the literature and recently many of the results were disputed⁴. We prepared our azines by condensing the hydrazone of 5-nitrofurfural with aromatic aldehydes. However this reaction did not proceed with aliphatic aldehydes or with ketones. In such cases the hydrazone of the other half was prepared first and condensed with 5-nitrofurfural. These reactions will be discussed.

* Lecturer

REFERENCES

1. DODD, M.C. AND STILLMAN, W.B., 1944, *J. Pharmacol. Exptl. Therap.*, **82**, 11.
2. "Introduction to the Nitrofurans", Eaton Laboratories 1958.
3. HABER, R.G. AND "ABIC LTD.", 1960, Israel Patent 13537.
4. UGRYUMOV, P.G. AND ZHUR, 1959, 2 *hur. obshchei Khim.*, **29**, 4091.

Gas chromatography of dienes with a dienophilic stationary phase

Y. HERZBERG-MINZLY* AND E. GIL-AV, *The Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth*

Butadiene, isoprene, the 1,3-pentadienes, the 1,3-hexadienes, 2,4-hexadienes and butadienyl acetylene have been subjected to gas chromatography, using chloromaleic anhydride as the stationary phase. These compounds, on passing through the column at 20–40°, undergo Diels Alder reaction, and as a result the portion of diene emerging from the column will vary with the flow of the carrier gas, due to change of contact time with the chloromaleic anhydride. Chromatographically the conversion of the diene can be followed conveniently by the decrease of its peak area.

The variation of the peak area with flow of carrier gas permits to recognize the presence of conjugated dienes in a chromatogram of a mixture of hydrocarbons, and further to distinguish between 1,3-dienes having different reactivity. The method has been applied to identify trans 1,3-dienes in the presence of their cis isomers.

The application of the method to the measurement of reaction rates of various classes of dienes is being studied.

Hydration of steroidal olefins by the hydroboration reaction

M. NUSSIM AND F. SONDHEIMER, *Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth*

A convenient modification of the Brown hydration method has been developed, involving hydroboration of an ethylene by means of lithium aluminium hydride, and boron trifluoride in ether followed by oxidation of the resulting alkylborane with alkaline hydrogen peroxide. The hydration of a variety of steroidal ethylenes has been accomplished by this procedure as well as by the original Brown method. Tri-substituted steroidal ethylenes have been shown to yield the corresponding secondary alcohols, whereas 1,2-disubstituted ethylenes give rise to comparable amounts of both possible positionally isomeric secondary alcohols. It has been shown that the reaction proceeds by over-all *cis*-addition of water from the less hindered side of the molecule. The hydroboration of steroidal conjugated dienes has also been investigated. Generally diols are thereby obtained (after oxidation), except in the case of $\Delta^{5,7}$ -dienes which yielded Δ^6 -ethylenes through 1,4-reduction.

* Lecturer

BOOK REVIEWS

THE PROTON IN CHEMISTRY By R.P. BELL, Cornell University Press, 1959. 223 pp.

The material included in this book describes mainly the new developments which occurred in the subject since the author's authoritative "Acid-Base Catalysis" appeared in 1941. The book includes chapters dealing in some detail with the theories of acids and bases; the effect of solvents on acid-base equilibria; the new developments in acid-base catalysis; the rates, equilibria and structures in acid-base reactions and the isotope effect in acid-base reactions.

The subject treated is by no means an easy one. Even the multiplicity of definitions by various schools is apt to cause confusion in the student. It is indeed a credit to R.P. Bell's lucid style of writing that he succeeds in giving his readers a complete account of the subjects he treats, without going into superfluous details — but nevertheless describing and explaining everything which the average reader, advanced student or research worker, should know about the subjects treated.

In many cases the attention of the reader is drawn to ambiguities in definitions, e.g., in defining the "strength" of a base like ammonia or an acid like carbonic acid (pp. 27–31). Similarly, the difference between the rate of ionization of a keto compound as distinct from its rate of enolization is emphasized and by this a subject which is very often confusedly treated even in the most recent literature, is clarified (pp. 144 ff.).

To quote only one more example out of many, the "tunnel effect" observed for protons is masterfully explained by an optical analogy, in a manner which makes this rather complicated phenomenon clear to anyone who is conversant with the dual nature (wave-particle) of light (pp. 205–7).

The quality of the printing, paper and binding is excellent and the book is singularly free of printer's errors. It can be most warmly recommended for all advanced students and research workers in all fields of chemistry, and it is practically a "must" for everyone interested in physical or in physical organic chemistry.

S. PATAI

*Department of Organic Chemistry,
The Hebrew University of Jerusalem*

ISOTOPIC TRACERS, By G.E. FRANCIS, W. MULLIGAN AND A. WORMALL, Second Edition, The Athlone Press, University of London, 1959. 524 pp.

The first edition of this textbook was written for undergraduate students taking the London Honours B.Sc. (Special Physiology). The present second edition was enlarged and brought up to date. It now includes a theoretical part, dealing in thirteen chapters with various aspects of the isotope tracer technique, e.g., the preparation of isotopes; the synthesis of labelled compounds; the properties, measurement and determination of stable and radioactive isotopes; the use of isotopic tracers in biological investigations in general and in the investigations of the kinetics of biological processes in particular.

The second part of the book describes a number of experiments using the tracer technique, assuming that the students have both counting equipment and mass spectographs available. This part consists of thirteen experiments. Finally, there are fifteen appendices, giving various relevant data, some special working methods, terms and definitions etc. etc.

The book is subtitled "A Theoretical and Practical Manual for Biological Students and Research Workers". Nevertheless, it is probably too large for undergraduates and too small for research workers.

A few rather disturbing errors were noted: On p. 79 it is stated that β -particle emission is caused by the conversion of a neutron to a proton within the nucleus, while on p. 476 a β -particle is defined as an electron, either negatively or positively charged. On p. 159, among a list of phosphors *p*-terphenyl and *p*-diphenylbenzene are listed as two different substances. An ion pair is defined as a

"negatively charged electron and a heavy positive ion" (p. 114) or, alternately, as "a singly charged gaseous ion together with the electron it has lost" (p. 482). On p. 311 the formula of cholin is given as a cation without the hydroxyl ion. On pp. 348-352 molecularity and reaction order are treated rather confusedly (... "a reaction ... is said to follow first order reaction kinetics, i.e., has the kinetic behaviour of a unimolecular reaction ..."). Finally, in this space-age it seems to be somewhat anthropocentric to define cosmic radiation as "a type of radiation *on the earth's surface*, originating in outer space (my italics; p. 481).

S. PATAI

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VISTAS IN FREE-RADICAL CHEMISTRY, In memoriam DR. MORRIS S. KHARASCH, Pergamon Press, London, New York, Paris, Los Angeles 1959. Edited by W.A. Waters F.R.S., 251 pp.

This book is devoted to the memory of the late Prof. M.S. Kharasch.

Kharasch was born in 1895 at Kremenetz, Ukraine, but from his early childhood he lived in the United States. He had an unusual professional career, gaining full Professor-rank as a young man and was actively connected not only with academic and industrial research, but also with scientific defence work; in all these varied fields of activity his contributions were outstanding and repeatedly earned him conspicuous honours. He died in 1957 in Copenhagen while on a mission on behalf of the United States Government.

Among the lasting contributions of Morris Kharasch to Chemistry are his fundamental investigations on free radicals which opened new fields in synthetic organic chemistry and strongly influenced the application of free radicals as catalysts in the chemistry of synthetic high polymers.

The book under review reprints twelve of the outstanding publications of Kharasch's. They are preceded by short biographical introduction, followed by a paper, contributed by W.A. Waters and F.R. Mayo dealing with the significance of the work of M.S. Kharasch in the development of free radical chemistry and with a survey of his published work showing the origin and relations of his many lines of research. It is correlated with a full list of his publications comprising 234 numbers. An indication of the exceptionally broad scope of his scientific interests is the subjects of the most important of his research as arranged in this bibliography of his publications:

Mercury compounds; the decomposition of unsymmetrical mercuriorganic compounds; a method of establishing the relative degree of electronegativity of organic radicals; the theory of partial polarity and related topics; the electron in organic chemistry; the chemistry of organic gold compounds; the peroxide effect in the addition of reagents to unsaturated compounds; other papers on addition of unsymmetrical reagents to unsaturated compounds; addition and substitution reactions of halogens; reactions of sulfuryl and other acid chlorides; reactions of atoms and free radicals in solution; the detection of free radicals in solution, the chemistry of hydroperoxides; polymerizations; other reactions involving oxidation of free radicals; factors determining the course and mechanisms of Grignard reactions; other papers and book on Grignard reactions and organo-metallic compounds; reactions in liquid ammonia; and papers on or relating to natural products followed by a number of unclassified papers.

The impact of M.S. Kharasch's work on organic chemistry can be judged by the following concluding papers of the book which deal with or touch on, some aspects of his work: The discovery of the Peroxide Effect by F.R. Mayo.-The Contributions of Morris S. Kharasch to Polymer Chemistry by C. Walling.- Some Trends in the Study of Free-radical Reactions in Solution by W.A. Waters.- The Chemistry of Free Radicals in the Gas Phase by K.O. Kutschke and E.W.R. Steacie.- Homolytic Aliphatic Substitutions by H.C. Brown.- Homolytic Aromatic Substitution by D.H. Hey.- Some New Chain Reactions Induced by Acyl Peroxides by G.A. Rusuwajew.- Electrophilic Addition to I:1:1-Trichloropropene by A.N. Nesmeyanov, R. Kh. Freidlina, L.I. Zakharkin, N.V. Kost, R.G. Petrova, A.B. Belyavsky and A.B. Terentiev.- The Reaction of Benzyl Ethers with Free tert-Butoxy Radicals by R.L. Huang and S.S. Si-Hoe.

This book fulfills admirably a twofold object: it pays fitting tribute to the memory of one of the

leading organic chemists of our time and it presents a balanced and up to date review on free radical chemistry, a field with which the name of Morris S. Kharasch is so intimately connected.

MAX FRANKEL

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HOMOLYTIC AROMATIC SUBSTITUTION By G.H. WILLIAMS, Pergamon Press, Oxford, 1960. vii + 133 pp., 45s.

Free radicals, being very reactive, lead to a large variety of side reactions and polymeric products which make it very difficult to trace the course of the substitution reactions and the relative amounts of isomeric products formed. For this reason, although free radical substitution reactions had been known for a relatively long time, no really quantitative work, which is dependable, as regards kinetic course and isomer ratios had been carried out until the last ten to fifteen years. The use of new analytical tools, such as various types of spectroscopy and gas chromatography had, in many cases, permitted the evaluation of homolytic aromatic substitution reactions from a more quantitative nature. These new results, in many cases, had been found to correspond more closely to the modern theories of organic chemistry, such as, the theories of molecular orbitals, free valence or atom localization energies.

The author, himself actively engaged in the field of homolytic aromatic substitution, exposes these facts in his present book. After brief introductory discussions of the modern theoretical approaches as regards mechanism, relative rates of reaction, and transition states, he discusses from the qualitative, preparative, and quantitative aspects the subject of homolytic arylation reactions, intermolecular arylation, such as the Pschorr reaction, alkylation, hydroxylation and the like.

The large amount of literature in this field is reviewed, and the author shows where the results are dependable, or correlate with modern theory. Where the same system was investigated by different authors, he points out, based on the different procedures followed, which results are more exact from a quantitative point of view. Remembering, that due to side reactions etc., the isolated products in most free radical substitution reactions never account for 100% of the starting material, the difficult task that the author faced in analyzing the results of different workers, sometimes controversial, and in drawing up conclusions, is fully appreciated.

The author reviewed the subject matter of homolytic aromatic substitution up to 1958, and pointed out in many places throughout the book where further research work may be carried out to clarify various problems.

The book is well written and ample references to the original literature are given. It should be highly recommended to those working on the organic chemistry of free radicals and to advanced students in organic chemistry.

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INTERNATIONAL SYMPOSIUM OF ORGANIC CHEMISTRY
Brussels
June 11—14, 1962

On the occasion of the 75th anniversary of its foundation, the Société Chimique de Belgique organizes in Brussels, June 11th-14th 1962, an *International Symposium of Organic Chemistry applied to the study of the Natural Products excluding Steroids and Polypeptides.*

The proceedings of this meeting, which will take place under the auspices of the International Union of Pure and Applied Chemistry (I.U.P.A.C.), will be divided into 5 Sections, as follows:

1st Section — Structure of new natural products

- a) Work completed or near completion
- b) Controversial structures

2nd Section — Methods used for the determination of chemical structures

- a) Analytical methods and chemical degradation
- b) Physical methods
- c) Stereochemical investigations (configurational and conformational)

3rd Section — Syntheses and chemical reactions (excluding degradation reactions)

- a) Stereospecific or highly stereoselective syntheses
- b) Stereospecific reactions

4th Section — Biosynthetic theories

- a) New hypotheses
- b) Extensions of classical theories
- c) Experimental studies
- d) Controversial theories

5th Section — Mode of action of naturally occurring compounds in biological processes

- a) Experimental studies
- b) Interpretation of experimental data.

Moreover, 7 general conferences are planned, i. e. 5 the subject of which will correspond to each of the Sections respectively, one plenary opening lecture and another for the closing of the Congress.

Secretary of the Symposium: Mr. Florent MARTIN, D.Sc. 68, rue Berkendael, Brussels 6 (Tel. 43.01.17 (225—255).

יוציא לאור ע"י
מוסד ויצמן לפרסומים במדעי הטבע ובטכנולוגיה בישראל
המועצה המדעית לישראל - משרד החינוך והתרבות - האוניברסיטה העברית בירושלים

Published by
THE WEIZMANN SCIENCE PRESS OF ISRAEL
Research Council of Israel, Ministry of Education and Culture
The Hebrew University of Jerusalem, Technion-Israel Institute of Technology
The Weizmann Institute of Science Bialik Institute

Printed in Israel
Raphael Haim Hacohen Press Ltd. Jerusalem